

IV. ENVIRONMENTAL DATA

Environmental Concentrations

No reports on the measurements of carbon black dust in the breathing zones of workers have been located. Most of the carbon black dust measurements have been from specific working areas within a particular plant, and involved the measurement of the total airborne dust rather than a particular carbon black or chemicals that may be associated with carbon black.

In 1961, Sands and Benitez [53] described the use of a high-volume sampler and a standard pleated filter to collect total dust in areas of the plants where carbon black was used. Results from their study are given in Table IV-1.

TABLE IV-1

TOTAL DUST CONCENTRATIONS (MG/CU M) IN ONE URUGUAYAN AND TWO US RUBBER PLANTS

Plant Locations	Uruguayan Plant	United States Plant A	United States Plant B
Banbury Loading	1.77-4.59	14.1-17.7	7.77-38.9
Milling	1.41-3.18	21.2	7.77-13.4
General air (Mill room)	0.14-0.28	1.06-2.12	1.06-4.24
Outside the plant	—	0.04-0.11	—

Adapted from reference 53

Generally, the concentrations were somewhat lower in the Uruguayan plant than in the US plants. The Banbury loading areas showed the highest concentration of total dust, ranging from 1.77 to 38.9 mg/cu m.

In April 1972, Kronoveter [54] performed a health hazard evaluation of a commercial warehouse, which had a total of approximately 200,000 sq ft of floor space. The carbon black storage area covered 10,000 sq ft. Samples of airborne dust in the carbon black storage area were collected on 37-mm diameter vinyl metricel filters and analyzed gravimetrically. The sample pump was operated at 1.7 liters/minute. All the air samples collected yielded airborne dust concentrations below the US Department of Labor standard of 3.5 mg/cu m for carbon black; the concentrations were below 0.8 mg/cu m.

From July 1972 to January 1977, the Occupational Safety and Health Administration [55] conducted 85 workplace investigations to determine compliance with the carbon black occupational exposure limit. Approximately 20% of the workplaces inspected were in violation of the 3.5 mg/cu m exposure limit (29 CFR 1910.1000), and about 60% of these were 1-2 times above 3.5 mg/cu m.

Sampling and Analysis

Occupational exposures to carbon black usually involve concomitant exposure to other airborne particulate materials. Present sampling and analytical technology does not allow for a reliable separation of carbon black from other airborne contaminants. Since there is no reliable method available for the separation of carbon black from other airborne contaminants, the total dust is usually measured as an indication of carbon black airborne contamination. Techniques for sampling airborne particulate material are well defined [56,57]. Membrane-filter sampling and high-volume sampling techniques have been applied to the collection of carbon black dusts in work environments [53,54].

With a high-volume sampler, Sands and Benitez [53] evaluated dust exposure in rubber factories where carbon black was used. The standard pleated filter used with this sampler was dried to a constant weight before use, and the dust samples collected on the filter were measured gravimetrically. High-volume samplers have the disadvantage that they usually cannot be positioned in the breathing zone of employees. Therefore, the actual employee exposure cannot be estimated as closely as it can be with personal sampling.

Kronoveter [54] conducted a health hazard evaluation of a carbon black storage area by collecting general, room air dust samples and weighing them. The dust samples were collected on 37-mm diameter vinyl metricel filters with the filters facing down and were taken at a sampling rate of 1.7 liters/minute. Measurements of general airborne dust concentrations may not indicate employee exposure adequately. The concentrations of carbon black dust close to a machine or process may be quite different from those in the breathing zone of an employee. Hence, collection of breathing zone samples is essential if one is to determine actual employee exposure. A breathing zone sampling device should be small enough to be conveniently attached to an employee's clothing without interfering with that person's work and should preferably contain no fragile glassware or liquids. Membrane-filter collection of dust using a battery-operated personal sampling pump satisfies these conditions.

Particulate separators are available for the determination of either mass or number concentrations [57]. In part because number concentration determinations, ie, counts of numbers of particles per unit volume, such as million particles per cubic foot (mppcf), usually require the

use of either laborious microscopic counting techniques or complex electronic counting equipment, mass concentration determinations by simple gravimetric methods are generally preferred. Instruments used for mass concentration determinations are in either of two broad categories, those with and those without a preselector (an elutriator, a cyclone, or other aerodynamic classifier). The preselector removes those particles that are larger than about 5 μm [57]. A mass concentration determination without the use of a preselector is generally referred to as a "total dust" concentration determination; use of a preselector is associated with "respirable dust" sampling [58,59].

Carbon black dust is mostly in the respirable range; particles of carbon black have diameters less than 0.5 μm , with those of most types of carbon blacks being smaller than 0.3 μm . Most industrial exposures of workers to carbon black during its manufacture or use involve activities during which carbon black is the predominant particulate species present; therefore, the use of a preselector during monitoring of these activities would be superfluous. At activities during which a variety of dusts may be generated, some airborne industrial dust in the general work environment would be expected to be in the respirable range; therefore, use of a preselector would not separate carbon black dust from other respirable dusts present. In this case, appropriate chemical treatment of a total dust sample might yield more meaningful data.

Norwitz and Galan [8], in 1965, reported procedures for determining the presence of carbon black and graphite in nitrocellulose-based rocket propellants. Their spectrophotometric method involved dissolving carbon black in boiling nitric acid to produce a solution whose yellow color comes from polycarboxylic acids with cyclic structures. The carbon black was first separated by dissolving the propellant in morpholine and filtering it through an asbestos mat. After the residue carbon black was washed with acetone, hot water, and hot hydrochloric acid, it was dissolved by boiling in nitric acid and measured spectrophotometrically at 540 nm. Since the color depends on the particle size of the carbon black, it was necessary to use the identical carbon black sample for the standard. Furthermore, some types of carbon blacks were only partially dissolved, even after boiling with nitric acid for 3 hours. No examinations of the suitability of this method for determining concentrations of airborne carbon black have been found.

Atmospheric carbon black concentrations have been usually determined by simple gravimetric methods [53,54,60]. Some investigators used predigestion with nitric acid to destroy organic matter, and then dried and weighed the residue containing free carbon black and insoluble inorganic matter [61]. The free carbon was then determined by the loss of weight on ignition between 140 and 700 C. Kukreja and Bove [62] modified this technique to determine lamp black collected on a high-volume, glass-fiber filter. Their procedure consisted of decomposing the glass-fiber mat with hydrofluoric acid, followed by dissolving insoluble inorganics and digesting organic material through the actions of ammonium hydroxide, nitric acid, and hydrochloric acid. The free carbon content was then determined by the difference in weight of the residue after heating first at 150 C and then at 700 C. These methods might be useful in the determination of airborne carbon black when other airborne particulate material is present. However, the methods have been tested only at concentration ranges well above the current Federal standard for carbon black (3.5 mg/cu m) [63]. In addition, the precision, range, and sensitivity of the methods were not presented in these reports, so complete appraisal of their suitability for determining airborne carbon black concentrations in the workplace is not possible.

From the available evidence summarized in Chapter III, carbon black apparently causes primarily pulmonary changes such as pneumoconiosis [12,14,15,17,18,25] and pneumosclerosis or pulmonary fibrosis [12-15,25]. Studies that have associated carbon black with pulmonary changes in the work environment have reported total dust concentrations rather than specific carbon black exposure concentrations. Carbon black particles are less than 0.5 μm in diameter [2], so they are therefore respirable. Also, over 90% of the particles in total dust samples from carbon black plants have been reported to be respirable [25]. Therefore, a preselector would not be useful. NIOSH [60] developed a gravimetric method for monitoring worker exposure to carbon black. A known volume of air was drawn through a tared polyvinyl chloride filter, and then the filter was dried to constant weight over a desiccant and weighed with a suitable microbalance. The method consists of drawing a known volume of air at 1.0-2.0 liters/minute through a tared 37-mm, 2.0- μm pore size, polyvinyl chloride membrane filter. The sample is measured gravimetrically after drying the filters over a desiccant to a constant weight. This method was validated over the range of 1.86-7.7 mg/cu m at atmospheric temperature and pressure ranges of 18-25 C and 749-761 mmHg, respectively, using a 200-liter sample. It has an estimated working range of 1.5-10 mg/cu m. The method was also validated for a 100-liter sample over the range of 7.8-27.7 mg/cu m. The method, although nonspecific and subject to interference from other particulate matter in the work environment, is simple and amenable for use with personal monitoring.

Because carbon black adsorbs PAH's, some of which are carcinogenic, it poses a risk of cancer. Also, since the adsorbed PAH's vary in type and in amount, based on both the type and grade of carbon black and the source of PAH's, a single environmental limit based on gravimetric determination of carbon black is not adequate to assess the risk of cancer development due to PAH's. Another method to selectively monitor contamination of the carbon black by adsorbed PAH's is therefore necessary.

In selecting a method to monitor the carbon black for PAH's, consideration has been given to specific analysis of such PAH components as benzo(a)pyrene or to extraction of the sample with a suitable solvent for measurement of total PAH's (actually, of total PAH's extractable by the selected solvent). The selection of total cyclohexane-extractable material, rather than analysis of one or more specific components, is based on the arguments presented in a review and analysis in a previous criteria document on Coal Tar Products [51].

As reviewed in that document as well as, in part, in the criteria documents on Asphalt Fumes [64] and Coke Oven Emissions [65], PAH's contain many substances often thought or known to be carcinogenic. The concentrations of specific compounds in any sample of PAH's are variable. In addition, as discussed in the document on Asphalt Fumes [64], there are many factors affecting tumors yields and carcinogenic responses, including either enhancement or inhibition of carcinogenesis by compounds within the same class of chemicals. These factors, and especially that pertaining to the great variability of concentration of any one component, argue for the more traditional method of extracting with a suitable solvent and expressing the airborne concentration in terms of solvent extractables. NIOSH [66] has concluded that benzene is especially hazardous and capable of causing leukemia, so, as was concluded in the criteria document on Coal Tar Products [51], cyclohexane extraction is recommended pending the definitive study of the analysis of airborne PAH's.

Thus, PAH content of carbon black should be analyzed by determining the weight of material extracted from filters by cyclohexane with the aid of ultrasonication.

Although a NIOSH validated method for sampling and gravimetric analysis of carbon black is available, a modified sampling and gravimetric analysis as described in the NIOSH criteria documents Criteria for a Recommended Standard...Occupational Exposure to Asphalt Fumes [64] and Coal Tar Products [51] is recommended so that both total carbon black and PAH's (cyclohexane extractable) can be determined in the same sample. The sampling and analysis methods described in Appendix I provide for the collection of total dust on a glass fiber filter with a silver membrane filter back-up. After collection of the sample, the weight of total particulates on the filter is determined by gravimetric analyses as also described in Appendix I. The final weight of the filter should be determined on the same balance that was used for determining the presampling weight. Before each weighing the filter should be equilibrated in a constant humidity chamber, and a static charge neutralizer should be attached to the balance to improve reproducibility of the weight determinations and thus enhance the gravimetric accuracy.

The filter pore size recommended is 0.8 μm . In the usual case of particulate sampling this pore size results in efficient collection. Smaller pore sizes will also collect efficiently, but there is concern over a possible increase in the pressure drop across the sampling train. Pore sizes significantly greater than 0.8 μm may cause a lesser efficiency in collection.

Engineering Controls

The major hazards encountered in workplace exposure to carbon black arise from the potential for respiratory disease [12-15,18,25] and from the problems associated with dermal contact [13,15,19]. Engineering controls should therefore be directed towards minimizing the potential for inhalation of and dermal contact with carbon black.

Because of the submicrometer particle size of most commercial carbon blacks, dusts generated at specific activities can be captured by an air stream with a relatively low velocity. However, the small particle size also means that a highly efficient collection system must be used to remove carbon black swept into a ventilation system. Manufacturers use elaborate baghouse collection systems for product recovery during the manufacture of carbon black [10]. Because of the physical properties of carbon blacks, eg, their small particle size and low density, the blacks tend to be ubiquitous in the work environment of both manufacturers and users until they are mixed with a containing material. Therefore, even when the environmental concentrations of carbon black are kept below the recommended limit, there may still be physical evidence that carbon black is present.

In general, local exhaust ventilation is more effective than general ventilation in controlling concentrations of airborne carbon black. Wherever a source of carbon black release into the worker environment exists, local exhaust ventilation can be used to minimize contamination of the general environment. General ventilation is important in areas not readily controlled by local exhaust ventilation. When exhaust ventilation is used, adequate makeup air, conditioned as needed for worker comfort, should be supplied. Good ventilation practices, such as those outlined in the current edition of Industrial Ventilation A Manual of Recommended Practice [67], published by the American Conference of Governmental Industrial Hygienists (ACGIH), should be followed. Design and operation guides can also be found in Fundamentals Governing the Design and Operation of Local Exhaust Systems (Z9.2-1971), [68] published by the American National Standards Institute (ANSI). To be useful, enclosures, hoods, and duct work must be kept in good repair so

that design airflows are maintained. All systems lose efficiency over time, so that it is necessary to monitor airflow regularly. Therefore, continuous airflow indicators, such as oil or water manometers, are recommended. Manometers should be properly mounted at the juncture of the fume hood and duct throat or in the ventilation duct and marked to indicate the desired airflow. Employers should establish a schedule of preventive maintenance for all equipment necessary to keep the environmental levels of carbon black at or below the recommended limit. Maintenance of a slight negative pressure throughout the dry carbon black handling systems aided in retaining the dust released when leaks and ruptures developed [10]. Mechanization, process enclosure, and bulk handling offer additional means of minimizing worker exposure to carbon black.

In the manufacture of carbon black, one of the dusty operations is the packing of carbon black in bags. Similarly, manually emptying the bags of carbon black also creates dusty environments. Bagging operations in manufacturing plants should be provided with local exhaust ventilation kept in good repair. Users of carbon black should install automated handling equipment if it is compatible with the process. If bag-size quantities of carbon black are essential, the user should ascertain whether the black could be packaged in a bag made of a material that is compatible with the process and thereby eliminate the necessity of opening and pouring from bags. If bags must be opened, the workers should be provided with suitable respirators when engineering controls, such as local exhaust ventilation, are not sufficient to control concentrations of airborne carbon black.

V. WORK PRACTICES

Most exposure to carbon black occurs in its production, particularly during pelletization, screening, bagging, hopper car loading, stacking, and unloading [10]. Exposure may also occur when equipment is cleaned, when leaks develop in the conveyor system, or when spills occur. The greatest carbon black release into the work environment was reported to occur when it was spilled before pelletization [10]. In tire manufacture, exposure to carbon black may occur from leaks in the conveyor systems and Banbury mixers or during maintenance operations. Good work practices and engineering controls should, therefore, be instituted to minimize or prevent inhalation or ingestion of or skin contact with carbon black during its production, processing, distribution, storage, and use.

In addition to implementing sound engineering controls, employers should institute a program of work practices that emphasizes good personal hygiene and sanitation. Such practices are important in preventing the possible development of cancer and the other effects on the respiratory system and skin associated with occupational exposure to carbon black. In addition, workers should be advised to shower or bathe after each workshift. If skin irritation is observed, the employee should be referred to a physician for appropriate medical care. Since carbon black may contain carcinogens and is very ubiquitous, the rest, eating, and smoking areas should be separated from the work areas.

Under normal operating conditions, respirators should not be used as a substitute for proper engineering controls. Respirators should only be used during emergencies, during nonroutine maintenance activities, and during the time necessary to test controls when appropriate engineering controls or administrative measures might not reduce the level of airborne carbon black to the permissible limit. Respirators conforming to Table I-1 and approved under 30 CFR 11 should be provided to employees, and a respiratory protection program should be established in compliance with the current Federal standard, 29 CFR 1910.134. Emphasis should be directed toward providing clean, well-maintained, well-fitted respirators for use in emergencies and unusual circumstances. The interior of the facepiece should not be contaminated by carbon black. The Respiratory Protective Devices Manual [69] and A Guide to Industrial Respiratory Protection [70] should be consulted for further information on respirators.

Respirators have been selected for inclusion in Table I-1 to protect against both the PAH's (cyclohexane extractable content) of the carbon black and the carbon black particles themselves. Concentrations greater than 3.5 mg/cu m have created a dark cloud [71] which would result in air concentrations so dense as might preclude the safe exit of employees in an emergency situation. The selection of the proper facepiece is difficult because of the possibility of particle buildup on the full facepiece that would impede adequate visibility. No reports were found that indicated that carbon black is an eye irritant. However, if eye irritation occurs, chemical safety goggles should be provided. Concentrations of cyclohexane extractables greater than 0.1 mg/cu m present an unacceptable risk with any respirator other than positive pressure, supplied-air or self-contained, full-facepiece respirators.

Skin irritation may be experienced by some workers exposed to carbon black [13,15,19] and might also result from the rigorous cleansing during the daily shower required after carbon black exposure. Employees experiencing skin irritation should be referred to a physician. Gloves or other personal protective equipment should be provided, used, and maintained in accordance with 29 CFR 1910.132-137. The protective equipment and clothing must be kept hygienic and uncontaminated and should be cleaned or replaced regularly. Employees should keep this equipment in suitable designated containers or lockers provided by the employer when the equipment is not in use.

Clean work clothing should be put on before each workshift. The proper use of full-body protective clothing requires a snug but comfortable fit around the neck, wrists, and ankles whenever the wearer is in an exposure area. At the end of the workshift, the employee should remove soiled clothing and shower before putting on street clothing. Street and work clothing should be separated within the change area. Clothing or other equipment must not be cleaned by blowing with air under pressure because airborne dust will be generated. Soiled clothing should be placed in a designated container and laundered before reuse.

Spills of carbon black should be promptly cleaned up by vacuuming and hosing down with water to minimize inhalation or skin contact. A plant-wide vacuum system may help to pick up spills and perform other cleanup and maintenance operations [10]. No dry sweeping or blowing should be permitted since only further contamination of industrial areas would occur. All waste material generated by the processes should be recycled or disposed of in compliance with local, state, and Federal regulations.

Although the NIOSH/OSHA Draft Technical Standard and Supporting Documentation for Carbon Black [72] warned against the dust explosion hazard of carbon black, other reports [73-76] suggested that carbon black presents only a moderate fire hazard rather than a dust explosion hazard. The ignition temperatures of carbon black dust explosions have been 445-890 C, and 35-74% oxygen was required [73]; hence, carbon black does not pose an explosion hazard in normal industrial environments. However, carbon black can sometimes be ignited following the careless use of open flames around carbon black, especially around carbon black packaged in paper bags [74]. Because carbon black burns slowly with little heat, carbon black fires tend to smolder and are difficult to detect. When carbon black fires do occur, carbon monoxide will be produced. Carbon black is electrically conductive, and dust collected on exposed electrical equipment might cause short circuits [74]. The National Electrical Code 1978 [75] classifies the presence of carbon black, charcoal, coal, and coke dusts with more than 8% total volatile material, or atmospheres containing these dusts sensitized by other materials so that they present an explosion hazard, as circumstances that require special precautions for safe performance of electrical equipment. However, none of the commercially available carbon blacks exceed 8% volatile content. Talmey [74] reported that carbon black, when mixed with dusts known to be explosion hazards, acts as an inert material, neither inhibiting nor promoting the propagation of the explosion. No data were presented to support this conclusion. Carbon black should be stored in leakproof containers in well-ventilated areas away from strong oxidizers. Sources of ignition, such as welding or other open flames, should be used cautiously in areas where carbon black is packaged or stored in bulk and should not be used when the carbon black is directly exposed to flames or sparks. Such measures are deemed essential because three workers died in a carbon black tank from the carbon monoxide given off by smoldering carbon black [77,78]. Evidently, sparks from a blowtorch used by the workers ignited a few bushels of carbon black.

Warning signs and labels indicating the respiratory and skin effects, ventilation requirements, and the potential for fire hazard should be placed on railroad cars used for bulk transport of carbon black and on bags containing the substance. In addition to these signs, posting should include additional warning signs to inform the employees where respiratory protection is needed and to alert them of the carcinogenic potential when the concentration of PAH's exceeds the recommended TWA limit. In all workplaces in which carbon black is handled, written instructions informing employees of the particular hazards of carbon black, the methods of handling it, procedures for cleaning up spills, and the use of personal protective equipment must be on file and available to employees. Employers may use the Material Safety Data Sheet in Appendix III as a guide to the information that should be provided.

To control the occupational hazards associated with exposure to carbon black, good work practices, personal hygiene, and proper training of employees are necessary. All new or newly assigned carbon black workers should receive on-the-job training before they are allowed to work independently. Employees must be thoroughly trained to use all procedures and equipment required in their employment and all appropriate emergency procedures. Employers should ensure that employees understand the instructions given to them. Employees should attend periodic safety and health meetings conducted at least annually by the employer and records of attendance should be kept by the employer.

VI. DEVELOPMENT OF STANDARD

Basis for Previous Standards

In 1965, the Threshold Limits Committee of the American Conference of Governmental Industrial Hygienists (ACGIH) proposed a Threshold Limit Value (TLV) of 3.5 mg/cu m for an 8-hour workday or 40-hour workweek for carbon black [63]. The 1966 Documentation of the Threshold Limit Values for Substances in Workroom Air [79] cited a number of reports to support the need for a TLV for carbon black. These reports were also cited in support of the TLV of 3.5 mg/cu m adopted by the ACGIH in 1967 [80]. Both the 1966 and 1971 editions of Documentation of the Threshold Limit Values for Substances in Workroom Air [79,81] cited the report by Sands and Benitez [53] as the basis for setting a workplace environmental limit for carbon black. Sands and Benitez [53] suggested a tentative limit of 3.5 mg/cu m as safe and practical for exposure to rubber mill room dust. Their suggestion was based on the concentrations of carbon black in the air of rubber factories in Uruguay and the United States. The documentations [79,81] also cited other studies, the usefulness of which in developing the recommendation for a TLV was not clear. For example, Ingalls and Risquez-Iribarren [22] conducted an epidemiologic study of the mortality and morbidity from all forms of cancers in workers engaged in carbon black production for up to 17.5 years and found that the incidence of and death rate from cancer were lower in the carbon black workers than in other working populations. Inhalation studies conducted by Nau et al [28] on monkeys and mice using channel black at 85 mg/cu m or furnace black at 56 mg/cu m for up to 7.7 years showed no malignancies in any of the exposed animals. The authors noted that dust accumulation in the lungs was the only significant result of carbon black exposure, although they found evidence in the ECG's of right atrial and right ventricular strain.

Von Haam and Mallette [37] found that some fractions of carbon black extracts were carcinogenic and that unfractionated extracts were not. Later, Von Haam et al [38] found that carbon black inhibited the activity of some carcinogens.

In 1976, the ACGIH [82] also recommended a short-term exposure limit (STEL) of 7 mg/cu m for carbon black. The STEL was defined by the ACGIH as an absolute ceiling not to be exceeded at any time during a 15-minute excursion period. It was proposed that no more than four excursions each day be permitted, with at least 60 minutes between excursions.

The 1977 publication of the International Labour Office on Occupational Exposure Limits for Airborne Toxic Substances [83] showed 3.5 mg/cu m to be the carbon black standard for Australia, Belgium, Finland, Italy, and the Netherlands. The report also listed carbon black limits for Switzerland as 20 mg/cu m for total dust and 8 mg/cu m for fine dust. No bases for these foreign standards have been found.

The present Federal standard is an 8-hour TWA concentration limit of 3.5 mg/cu m measured as total dust (29 CFR 1910.1000). This environmental limit was adopted from the 1968 ACGIH TLV.

Basis for the Recommended Standard

(a) Permissible Exposure Limits

Almost all reports of human exposure to carbon black deal with effects on workers who make carbon black. No reports were found on the effects on health of exposure to carbon black during manufacture of tires for automotive vehicles or in other uses, such as in the production of inks, paints, plastics, and ceramics. None of the reports of effects on human health of exposure to carbon black listed the concentrations of airborne carbon black, but the total dust concentrations of the work environment ranged from 8.2 mg/cu m [25] to 1,000 mg/cu m [13].

A number of reports [12-15,18,25] demonstrated that the major effects of carbon black are respiratory. In workers engaged in carbon black production, lung diseases found, in descending order of prevalence, were varying degrees of pneumoconiosis [12,14,15,18,25], pneumosclerosis or pulmonary fibrosis [12-15,25], bronchitis [13,14,18,25], emphysema [14], and tuberculosis [12,18]. No evidence that demonstrated that exposure to carbon black influenced susceptibility to active tuberculosis was presented. Pneumoconiosis and pulmonary fibrosis are the only two of these diseases that seem to be related to exposure to carbon black. Structural changes in the lungs have been accompanied by functional changes exemplified by decreased vital capacity, respiratory minute volume, maximum ventilatory capacity, FVC, and FEV₁ [14,15,18,25]. Coughing, breathing difficulties, and pains near the chest and heart were accompanied in some workers by lung afflictions [14,15].

Respiratory effects consonant with pneumoconiosis and emphysema found in workers exposed to carbon black were also observed in mice and monkeys exposed to channel black at 85 mg/cu m or furnace black at 56 mg/cu m for up to 1.78 years [28]. In addition to the dust accumulation in the upper and lower respiratory tract, thickening of the alveolar walls and occasional cellular proliferation were also seen in these exposed animals. An increased concentration of hydroxyproline in the lung, indicating the development of collagen and thus thought by the authors to be indicative of developing fibrosis, was noted in one of the studies [18] when 50 mg of carbon black was administered intratracheally to rats.

Dermal effects on workers exposed to carbon black have been identified in three reports [13,15,19]. Komarova [13] noted that 92% of more than 80 workers exposed simultaneously to dust at 10-1,000 mg/cu m and to carbon monoxide at 5-120 mg/liter in the packaging department of a carbon black plant complained of skin irritation. In another study, Komarova [15] found that some of 643 workers engaged in furnace black production had skin diseases. In the work area, 75% of the air samples taken contained dust in concentrations greater than 10 mg/cu m, 74% of the samples contained carbon monoxide in concentrations exceeding 20 mg/cu m, and 13.5% of the samples had concentrations of hydrocarbons in concentrations greater than 300 ppm. Capusan and Mauksch [19] reported that, during a period of 5 years, 53-86% of the workers producing carbon black by large-scale sooting of a wick burning hydrocarbon and naphthene (cycloparaffin) wastes developed specific dermatoses, eg, stigmata with fissured keratosis and linear tattooing, while an additional 7-16% had nonspecific dermatoses.

In mice, exposure to furnace black at 56 mg/cu m for up to 1.78 years caused atrophy or hyperplasia of the epidermis, fibrosis of the dermis, or both, but these were not seen consistently;

mice exposed at 85 mg/cu m for up to 1.78 years consistently showed subcutaneous edema [28].

Two reports described effects on the heart of workers who produced carbon black [13,15]. Komarova [13] reported that, of more than 80 workers exposed to dust at 10-1,000 mg/cu m and to carbon monoxide at 5-120 mg/liter during packaging of carbon black, 50% had signs of myocardial dystrophy. In another study, Komarova [15] noted diseases in the cardiovascular system in 75% of 643 furnace black production workers. Dust concentrations in their work environment exceeded the MPC of 10 mg/cu m in 75% of the samples taken, while the MPC's for carbon monoxide and hydrocarbons were exceeded in 74 and 13.5% of the samples, respectively.

Animal experiments revealed that effects on the heart can be found after prolonged exposures to carbon black [28,30]. The ECG's of monkeys exposed to channel black at 85 mg/cu m for 0.59-0.89 year or to furnace black at 56 mg/cu m for 1.49 years revealed right atrial and right ventricular strain [28]. In addition, morphometric analysis of monkeys exposed at thermal black concentrations of 53 mg/cu m for 3.35 years showed right ventricular, septal, and left ventricular hypertrophy [30]. After 0.89 year of exposure to furnace black at 56 mg/cu m or to channel black at 85 mg/cu m, the heart-to-body weight ratios of exposed mice were slightly higher than those of the controls.

Keratoses and leukoplakias were found in 26 and 36 workers, respectively, among 300 persons exposed to carbon black [26]. These lesions were found primarily in the areas of dust accumulation. This report also showed that pretumorous oral lesions can be produced experimentally by exposing mice to carbon black. The concentrations of carbon black or total dust in the work environment were not given.

Human studies have found no changes other than those in the lungs, heart, oral mucosa, and skin. However, exposure of mice to channel black at 85 mg/cu m or to furnace black at 56 mg/cu m for up to 1.78 years caused amyloidosis of the liver, spleen, and kidneys.

Three reports [20-22] were found that presented possible evidence of a carcinogenic potential of exposure to carbon black. Maisel et al [20] reported a case of cancer related to carbon black exposure that occurred in a 53-year-old research chemist who was exposed to many types of carbon black for 11 years. The chemist had parotid duct carcinoma, and the excised tissue revealed squamous-cell metaplasia and black material. The black material was assumed to be carbon black but was not identified so that no firm conclusion can be reached on the role of carbon black in the production of carcinoma of the parotid duct in this individual. From the epidemiologic surveys conducted on employees who made carbon black, Ingalls and Resquez-Iribarren [21,22] identified four cases of melanoma of the skin. Although these preliminary findings suggest a cause for concern that a melanoma type of skin cancer might develop in workers exposed to carbon black, further studies are needed to evaluate the cancer risk involved in occupational exposure to carbon black.

In a number of studies conducted by Nau and coworkers [28,30,39,41], administration of whole furnace, thermal, or channel black by oral, inhalation, dermal, or sc routes did not produce cancer in mice. However, when benzene-extractable materials from channel and furnace blacks were administered to mice by skin painting [37,39], sc injection [42], or feeding [38,41], malignant

tumors were produced. In addition, Falk et al [45] showed that incubation of a commercial carbon black with sterile human plasma for 1.5-192 hours resulted in the elution of varying amounts of pyrene, fluoranthene, 1,2-benzpyrene, 3,4-benzpyrene, 1,12-benzperylene, anthanthrene, and coronene.

Most carbon black particles are reported to be less than 0.5 μm in diameter [2] and hence are respirable. Available reports indicate that the effects of exposure to carbon black at dust concentrations of 8.2 mg/cu m or above for more than 10 years are qualitatively and quantitatively similar to those of exposure to nonspecific respiratory irritants, causing primarily pneumoconiosis or pulmonary fibrosis. In addition, inhalation exposure of animals to carbon black caused changes in the liver, spleen, and kidneys [28]. Concern for employee health requires that possible acute and chronic effects of carbon black, specifically pneumoconiosis, pulmonary fibrosis, skin irritation, fissured skin keratosis, linear tattooing, and myocardial dystrophy, be minimized.

The present Federal environmental limit of 3.5 mg/cu m is based on the 1968 TLV, which in turn was based, as was discussed above, on the airborne concentrations found to exist in rubber factories, but without apparent evidence of safety data. The findings of Nau and coworkers [28] of skin effects and emphysema in mice and heart strain and emphysema in monkeys are not completely persuasive because of the lack of significance of the association between local effects on the skin and airborne contamination and because of a question of intercurrent diseases having played a part in the lung and heart lesions. But the implications of the study are reinforced by the other evidence reviewed earlier in this Chapter and in Chapter III of systemic effects (heart and lung) of carbon black. Since there is inadequate information available to associate carbon black exposure concentrations corresponding to the present Federal limit there has not been identified an effect that can be directly attributed to carbon black exposure at concentrations less than 3.5 mg/cu m. Further research is necessary to resolve whether or not carbon black poses a potential safety hazard due to decreased visibility at airborne concentrations of 3.5 mg/cu m. Therefore, the present 3.5 mg/cu m limit should be maintained pending further investigations on carbon black exposure.

To differentiate between PAH-containing carbon black, it is proposed to determine (by solvent extraction) whether the carbon black contains 0.1% (W/W) PAH or more. A concentration of 0.1% is selected on the basis of professional judgment, rather than on data delineating safe from unsafe concentrations of PAH's. This concentration limit has also been used in some of the 29 CFR 1910 standards (4-nitrophenyl, 1910.1003; 2-naphthylamine, 1910.1009; and 4-aminodiphenyl, 1910.1011) to help differentiate carcinogen-contaminated materials from those not considered contaminated. In addition, it appears to be a feasible limit, exemplified by data in Table XII-1 on concentration of benzene-extractables in some samples of carbon black. This limit of 0.1% is also very conservative, in that it could result in an airborne concentration of PAH's of 0.035 mg/cu m (as cyclohexane extractables) when the carbon black was at its proposed environmental limit of 3.5 mg/cu m. While this concentration of 0.035 mg/cu m is significantly less than the recommended limit of 0.1 mg/cu m for airborne cyclohexane extractables, it should be noted that this 0.1 mg/cu m limit was justified on the basis of feasibility of measurement, not on a demonstration of its safety.

Various studies have shown that PAH's are adsorbed on carbon black [3,5,6,15,16,32,45]. The concentration range for 3,4-benzopyrene adsorbed on carbon black was 6.5-345 ppm and was 92-472 ppm for corone [3,5,6,16]. Some of the PAH's associated with carbon black, such as

3,4-benzpyrene, have been indicated to be carcinogens [6,84]. Furthermore carbon black has been capable of increasing retention within respiratory tract of 3,4-benzpyrene when 3,4-benzpyrene adsorbed on carbon black was injected intratracheally [32,33]. The desorption of adsorbed PAH's from carbon black may occur under various conditions. Such desorption may occur in work environments with elevated temperatures or solvent vapors [16]. The PAH's may be eluted from carbon black by human blood plasma [45,46] and under certain health conditions, such as acute respiratory infections [48]. These reports suggest a potential risk of development of cancer against which carbon black workers should be protected. A working environment adhering to the recommended environmental limit for carbon black may not protect workers from a potential cancer risk due to the adsorbed PAH's, because their concentration in carbon black dust depends on the type and grade of carbon black as well as the characteristics of the PAH's. Therefore, a 10-hour TWA limit of 0.1 mg/cu m, measured as the cyclohexane extractable fraction, is recommended to protect against the risk of cancer development due to the PAH's adsorbed on carbon black. The rationale in choosing the recommended TWA limit for cyclohexane extractables is chiefly based on methodologic limitations, ie, it is the least concentration reliably detectable; this point has been more thoroughly discussed in the NIOSH document Criteria for a Recommended Standard....Occupational Exposure to Coal Tar Products [51].

(b) Sampling and Analysis

Personal sampling with glass-fiber and silver membrane filters is recommended to collect and monitor airborne carbon black in the work environment. A method involving weighing of total dust is recommended for analysis of the particulate matter collected on the filters. The recommended sampling and analytical method is simple and amenable to assessing workers' breathing zones by personal sampling. Although it is nonspecific in that it will measure all particulate matter in the work environment, in the absence of an alternative analytical method that is specific for determining carbon black, this sampling and analytical method, described in detail in Appendix I, is recommended for assessing employee exposure. To monitor exposure to PAH's, one should determine the weight of material that can be extracted by cyclohexane from the filters with the aid of ultrasonication as described in Appendix II.

(c) Medical Surveillance and Recordkeeping

Preplacement medical screening is recommended to identify, and to establish baselines for, preexisting conditions that might make a worker more susceptible to adverse effects of substances in the work environment.

Chapter III reviewed the possible effects of exposure to carbon black; in the discussion in Correlation of Exposure and Effect, it was concluded that exposure to carbon black might cause pneumoconiosis and pulmonary fibrosis, ECG changes, and dermatoses. In addition, PAH-containing carbon black may cause premalignant changes in the oral mucosa (keratosis and leukoplakia) and there is experimental evidence [32] suggesting lung cancer as a possible consequence of carbon black exposure [32]; in addition, there is suggestive but inconclusive epidemiologic evidence of skin cancer and of leukemia. Therefore, physical examinations should include in the case of PAH-free carbon black exposure chest X-rays and ventilatory function tests, ECG's and careful examination of the skin. Additional examinations should be included if employees are exposed to PAH-containing carbon black to detect for possible changes in the oral mucosa; cytologic examination of sputum should also be considered, especially in cases of

unexplained findings on radiologic examination. While the evidence that PAH-containing carbon black causes leukemia is only suggestive, complete blood counts are a desirable part of a complete medical examination.

The evidence that carbon black exposure causes bronchitis and emphysema is less convincing than that implicating carbon black in the causation of pneumoconiosis and fibrosis. However, a medical surveillance program designed to detect pneumoconiosis should also detect emphysema and bronchitis, if they are present and a consequence of exposure. It is expected, of course, that detection of toxic effects through a diligent program of medical surveillance will result in steps to improve hygiene or work practices, and thus result in reduction of exposure.

Thus, all employees occupationally exposed to carbon black should be examined prior to placement by chest X-ray and ventilatory functions tests, ECG, and careful examination of skin and oral mucosa, whether the carbon black is PAH-free or not. In the case of periodic examinations, chest X-rays should be taken annually if the carbon black contains more than 0.1% cyclohexanone extractable material or every 3 years if the carbon black contains 0.1% cyclohexane extractable material or less, and pulmonary function tests, ECG's and examination of the skin and oral cavities of workers will help detect any occupationally related illness that might otherwise go undetected because of either delayed toxic effects or the subtlety of the changes. Special medical attention should be given to workers exposed to carbon black containing more than 0.1% cyclohexane extractable material, because of the possibility of neoplasms of the skin, oral mucosa or respiratory tract.

There are likely limitations on the number of sputum cytology examinations which can be accomplished by the facilities now available. Efforts should be made to increase the number of qualified laboratories available for routine analysis of cytologic specimens; these efforts should standardize procedures and increase the feasibility of performing these examinations.

Because of the usually slow development of cancer, all medical records should be maintained for at least 30 years beyond the duration of employment.

(d) Personal Protective Equipment and Clothing

Since carbon black particles are respirable and affect the upper and lower respiratory tract [12-15,18,25] and oral mucosa [26], and since the PAH's adsorbed on carbon black are potentially carcinogenic, respiratory protective measures are recommended. Proper engineering controls should be the primary means of reducing the atmospheric concentrations of carbon black in the work environment.

Respirators should be used only during emergencies and during nonroutine repair and maintenance activities when the airborne carbon black and PAH levels might not be reduced by appropriate engineering controls or administrative measures to below their respective TWA limits. If eye irritation occurs as a result of exposure to carbon black, chemical safety goggles should be worn. Carbon black exposure has been reported to cause skin irritation in some workers [13,15,19], so that gloves, other appropriate skin protection, and personal full-body work clothing resistant to penetration by carbon black are recommended. These should be required in work with PAH-containing carbon black.

(e) Informing Employees of Hazards

A continuous education program is an important part of a preventive hygiene program for employees occupationally exposed to carbon black and the sometimes associated PAH's. Properly trained persons should apprise employees at least annually of the possible sources of exposure to carbon black, the adverse effects associated with such exposures, the engineering controls and work practices in use and being planned to limit such exposures, and the procedures used to monitor environmental controls and the health status of employees.

Employees also need to be instructed in their responsibilities, complementing those of their employers, in preventing effects of carbon black on their health and in providing for their safety and that of their fellow workers. These responsibilities of employees apply primarily in the areas of sanitation and work practices, but attention should be given in all relevant areas, so that employees faithfully adhere to safe procedures.

(f) Work Practices

Engineering controls and good work practices must be used to minimize worker exposure to carbon black. Since carbon black affects chiefly the respiratory system, efficient local and general ventilation, maintenance of a slight negative pressure throughout dry carbon black handling systems, and process automation or mechanization should help reduce the concentrations of carbon black and adsorbed PAH's in the work atmosphere. Adoption of these measures will lessen the possibility of skin contact or accidental ingestion.

Because of the risk of developing cancer and in the interest of good hygiene and work practices, it is recommended that storing, handling, dispensing, and eating of food be prohibited in all carbon black work areas, regardless of the concentrations of carbon black or PAH's. In addition, it is recommended that employees who work in carbon black work areas wash their hands thoroughly before using toilet facilities, eating, or smoking. Employees should also shower or bathe using soap or other skin cleansers at the end of each workshift before leaving the work premises.

(g) Monitoring and Recordkeeping Requirements

Samples of bulk carbon black should be analyzed for PAH's by extracting with cyclohexane (see Appendix II). When the concentration of cyclohexane extractables is negligible, judged to be 0.1% or less, it can be assumed for practical purposes that the carbon black is PAH-free. Possibly vendors of PAH-free carbon black will certify its low PAH concentration (it is understood that a patent for a process to make such carbon black has been applied for). If only PAH-free carbon black is used and there are no other significant sources of airborne PAH's, such as operations with coal tar products, there will not be occupational exposure to PAH's and those parts of the recommended standard applying to occupational exposure to PAH-containing carbon black need not be followed. Therefore, occupational exposure to PAH-containing carbon black should be defined as any work in which there is contact with carbon black in bulk or airborne, containing more than 0.1% cyclohexane extractable material. In the case of PAH-free carbon black, an action level of half of the environmental limit of 3.5 mg/cu m as a TWA concentration for a 10-hour workshift for a 40-hour workweek is proposed. Occupational exposure to PAH-free carbon black is defined as exposure to a TWA concentration greater than the action level.

To characterize each employee's exposure, personal air sampling and analysis for carbon black and PAH's must be conducted. This procedure should be repeated at least every 6 months and whenever environmental or process changes occur. To relate the employee's known occupational exposure to effects that may not appear during the period of employment, employers should keep records of environmental monitoring for the same 30-year period as the medical records. This is consistent with the provisions of the Toxic Substances Control Act.